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Analysis of Ambient Polar Volatile Organic Compounds Using Chemical Ionization-Ion Trap Detector

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A promising technique for measuring polar VOCs is chemical ionization GC/MS (GC/CI-MS) in the quadrupole ion trap. This approach allows whole air samples to be taken since the water present in the air is used as the CI reagent gas. Water CI leads to appreciable intensities for the proton transfer agent H_3O^+, which produces intense pseudomolecular ions and class-specific fragmentation patterns for various low molecular weight polar compounds.

Standard mixtures of polar species at low concentrations in humidified zero air were analyzed without a membrane dryer, using a cryogenic trap and CI-GC/MS with the ion trap detector in the full scan model. Water appears to be an effective CI reagent gas in the ion trap, and the GC/CI-ITD system can exploit the water vapor normally present in ambient air to circumvent the problems usually encountered in a humid matrix.

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ABSTRACT

The current approach to measuring trace levels of volatile organic compounds (VOCs) in ambient air requires cryogenic trapping of the analytes, followed by thermal desorption and low-temperature refocusing onto a column for analysis by capillary gas chromatography/mass spectrometry (GC/MS). This approach has been successfully applied to nonpolar VOCs, but its use for more polar species has been complicated by the problems associated with the ambient water vapor collected with the VOCs.

A promising technique for measuring polar VOCs is chemical ionization GC/MS (GC/CI-MS) in the quadrupole ion trap. This approach allows whole air samples to be analyzed since the water present in the air is used as the CI reagent gas. Because of the variability of ambient water vapor levels, an externally mounted water reagent source is used to maintain a constant reagent gas pressure for CI experiments. Water CI leads to appreciable intensities for the proton transfer agent H_3O^+, which produces intense pseudomolecular ions and class-specific fragmentation patterns for various low molecular weight polar compounds. Using water CI enhances sensitivity by a factor of about 5, as is apparent from a comparison of CI and electron impact intensities obtained with the Finnigan MAT 800 Ion Trap Detector (ITD).

In this preliminary study, mixtures of polar species at low concentrations in humidified zero air were analyzed without a membrane dryer, using a cryogenic trap and CI-GC/MS with the ion trap detector in the full scan mode. Water appears to be an effective CI reagent gas in the ion trap, and the GC/CI-ITD system can exploit the water vapor normally present in ambient air to circumvent the problems usually encountered with a humid air matrix. The water vapor in the samples does, however, have a deleterious effect on the quality of the chromatography achieved. Future work should focus on optimizing the analytical technique and evaluating its suitability for various polar compound classes.

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SECTION 1

INTRODUCTION

Increasing public concern over polar volatile organic compounds (VOCs) of low molecular weight has spurred the current interest in developing better measurement techniques for these compounds. Some polar VOCs are often the subject of nuisance complaints from the public (e.g., alkylthiols, amines, aldehydes, etc.), while others are cited as potentially toxic compounds from industrial emissions (e.g., ethylene oxide, propylene oxide, acrolein, etc.). Analysis of trace levels of polar VOCs in air, however, poses many problems and, at present, the nature and distribution of these compounds in the atmosphere cannot be adequately characterized.

By contrast, the method for determining a large number of nonpolar volatile organic compounds in air is well established. Stainless steel polished sampling canisters are used with a combination of cryogenic trapping and high resolution gas chromatography (GC) coupled to a suitable detector, such as flame ionization, electron capture, or mass spectrometry (GC/MS).[1] Cryogenic trapping preconcentrates the analytes by first passing the gaseous sample through a cold tube in which the organic components condense on the cold surface; the condensate is then desorbed and analyzed by GC. Mass spectrometry, because of its high level of specificity, is used when high quality ambient data are required.[2]

The methods currently used to determine polar VOCs have their origins in industrial hygiene technology and rely primarily on liquid impinger sampling. These methods are generally restricted in sensitivity to levels at parts-per-million by volume (ppmv). Some progress has been made in measuring aldehydes at levels of parts-per-billion by volume (ppbv) by collecting the compounds on a silica gel substrate coated with dinitrophenylhydrazine and then analyzing the hydrazones formed by high-performance liquid chromatography.[3]

In general, however, attempts to sample polar VOCs at trace levels have been ineffective due to their greater chemical reactivity, affinity for surfaces, and tendency to undergo polymerization.[4] The analytical problem has been exacerbated, especially for GC/MS measurements, by co-collected water vapor, which occurs at concentrations that are several orders of magnitude greater than those of the analytes.[4,5]

The moisture problem has been overcome for many nonpolar compounds by incorporating a drying step before GC analysis.[5] The air sample passes through a Nafion membrane dryer tube before being cryogenically concentrated; water vapor in the air stream permeates the dryer walls while most of the air pollutants of interest pass through the tube. This technique is limited, however, to relatively nonpolar compounds since small polar molecules, such as alcohols, aldehydes, and ketones, also permeate the walls of the drying tube to some extent.[4]

Pleil et al.[6] recently developed a method that avoids the need for preconditioning the sample with membrane dryers. Using a megabore column, a slow temperature program to gradually release the water trapped on the column, and GC/MS in the full scan mode, they were able to analyze several polar compounds at low levels in a humidified air matrix. Sensitivity was lost, however, because of the presence of water in the MS source and the slow temperature program, which caused the peaks of the more volatile compounds to broaden.

A promising technique for measuring volatile polar compounds in whole air samples is chemical ionization GC/MS (CI-GC/MS) in the quadrupole ion trap,[7,8] using the water present in the air as the chemical ionization reagent gas. This approach has been exploited extensively in the atmospheric pressure chemical ionization triple-stage quadrupole mass spectrometer (APCI-MS/MS).[9] The trace amounts of water present in the carrier air sample lead to appreciable intensities for the solvated proton $H^+(H_2O)_n$, with the range of n depending on the partial pressure of the water.[10]

Using a conventional single-stage quadrupole GC/MS system, Hawthorne and Miller[11] recently showed that water CI produces intense pseudomolecular ions and class-specific fragmentation patterns for aliphatic and aromatic aldehydes, ketones, esters, and carboxylic acids. They found that water CI also gives a roughly 200:1 selectivity for these carbonyl species over alkanes. This is particularly advantageous when attempting to measure polar compounds in ambient air, which is usually dominated by alkanes. Compounds such as the thiols and sulfides, which are also of interest in air pollution studies, have proton affinities in the same range as these carbonyl compounds,[10] so they would be expected to also undergo protonation when analyzed with water as the CI reagent gas.

To date, the chemical ionization capabilities (ARC--Automatic Reaction Control™ mode) of the Finnigan MAT Ion Trap Detector™ (ITD) have been investigated in detail for the reagent gases ammonia, methane, and isobutane.[12,13] As opposed to CI in a conventional MS ion source, CI in the ITD requires only 10^{-6} to 10^{-4} torr of reagent gas.[8] This low pressure is sufficient to convert sample molecules to ions with high efficiency because of the long reaction times (milliseconds) in the trap. The ion trap operates in a pulsed mode; a special sequence of rf voltages and time intervals are used to select the reagent ions, then react them with the sample to form analyte ions before the rf voltage is scanned for mass analysis.

A recent study has shown that chemical ionization in the trap can improve the lower detection limit for some compounds by as much as a factor of 10 over that for electron impact (EI) ionization.[8] The relatively low cost and exceptional sensitivity of the ITD make it an ideal candidate detector for the analysis of polar VOCs of environmental interest.

With these considerations in mind, the major objective of this preliminary investigation has been to determine and optimize, using GC/CI-ITD in the full cyclic scan mode, the conditions under which water chemical ionization can be used for the analysis of selected polar VOCs in whole air samples. In this report, we describe the instrumentation used, and discuss laboratory experiments designed to test the suitability of the system for the

analysis of polar VOCs in humidified air. Electron impact and water CI mass spectra for several representative polar compounds are compared, and the effects of humidified air and dry air on the CI-ITD analysis of the polar and some nonpolar compounds are discussed.

SECTION 2

CONCLUSIONS

A system that uses GC/water chemical ionization with the Finnigan MAT Ion Trap Detector has been tested in the laboratory for the analysis of polar VOCs in humid air matrixes. The preliminary laboratory experiments indicate the following:

* The analysis of polar VOCs is fraught with difficulties and needs to be dealt with by compound class.

* Water appears to be an effective CI reagent gas in the ion trap. Its proton affinity is low enough to allow it to react with a wide range of polar VOCs.

* The ITD permits the use of the very long reaction times necessary to detect low sample concentrations with high sensitivity.

* The GC/CI-ITD system can exploit the water vapor present in the air, thus circumventing the problems normally encountered when analyzing humid air for these compounds, as with the membrane dryer.

* The presence of water vapor in the air has a deleterious effect on the quality of the chromatography achieved.

SECTION 3

RECOMMENDATIONS

Laboratory tests have been conducted to evaluate the effects of humid air matrixes on the analysis of polar VOCs using water chemical ionization with the Finnigan MAT Ion Trap Detector, coupled with cryogenic trapping, to preconcentrate the VOCs. It is recommended that future work should focus on the following:

* The effect of instrument operating conditions on sample precision should be determined.

* Investigate the use of significantly smaller whole air samples to further reduce the deleterious effects of humidified air on the trace-level analysis of polar VOCs. (The Ion Trap Detector with water chemical ionization is exceptionally sensitive.)

* Investigate the use of smaller sample volumes and alternative chemical ionization reagents, such as isobutane, (Isobutane CI gives rise to less fragmentation of the molecular ion than is obtained with water, resulting in higher sensitivities.)

* Carefully evaluate chromatographic performance problems associated with the analysis of polar volatile organic compounds in the presence of water vapor.

* Further develop a suitable sample calibration and delivery system for polar VOCs.

SECTION 4

EXPERIMENTAL

INSTRUMENTATION

The system used for sampling and analyzing VOCs consisted of a semi-automated cryogenic sampler (Nutech Model 3538-02) and a Finnigan MAT 800 Ion Trap Detector. Figure 1 is a diagram of the system.

Sampling System

The sampling system has been described in detail elsewhere.[1,2] Briefly, it consists of a Nutech Model 3538-02 cryogenic trapping and desorption unit and a Nutech Model 320-01 temperature controller.

The gaseous sample to be analyzed (either from a canister or from a special sample delivery system) and the zero-grade helium used to flush the trap during desorption are connected to the trap through a Valco six-port air actuated valve (Model A2N6WT), which controls switching between the two. The valve/trap assembly is housed in a heated enclosure. Sample flow through the trap is regulated with a Tylan (Model FC-260) mass flow controller.

Normally, whole air samples collected in canisters are preconcentrated by passing them through the cryogenic trapping system prior to analysis. To investigate the effects of ambient water vapor on the analysis of polar VOCs, a special sample delivery system was constructed.[6] This system, which was used in lieu of canisters for whole air samples, allowed us to generate sample mixtures of polar compounds in dry zero air or humidified zero air. Samples were injected into a dry zero-grade air stream through a septum. Humidified samples were prepared by first passing the air through a flask partially filled with water, while dry samples were generated by bypassing the humidifier. The experimental system is shown in Figure 2. The relative humidity of the gas stream was measured with a YSI Model 91HC Dew Point Hygrometer.

Experiments were also carried out to demonstrate the effects of removing water from a humidified gas stream on the analysis of polar VOCs. A Nafion membrane dryer tube (Perma-Pure Model MD 125-48F; shell and tube configuration) was installed between the sample delivery system and the trapping system.[5] A countercurrent flow of dry argon was used to purge the shell of water vapor.

Analysis System

A Varian 3400 GC was equipped with a split/splitless injector and a 60 m x 0.32 mm i.d. fused silica capillary column (J&W DB-1701) with a film thickness of 0.2 μm. The column flow was maintained at 1 mL/min; zero-grade helium was used as the carrier gas. The column outlet was attached directly via a heated (250°C) transfer line to a Finnigan MAT 800 Ion Trap Detector.

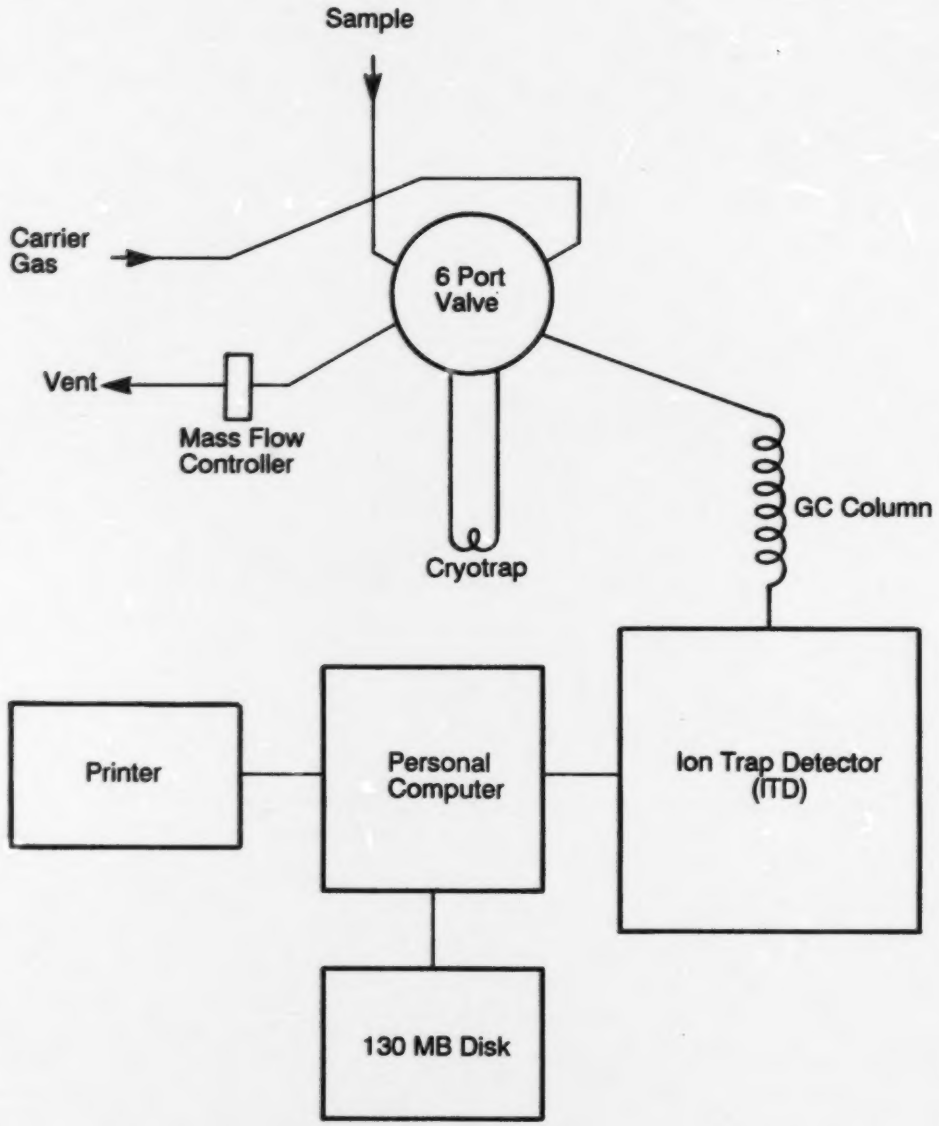

Figure 1. Diagram of trapping and analysis system for gaseous samples.

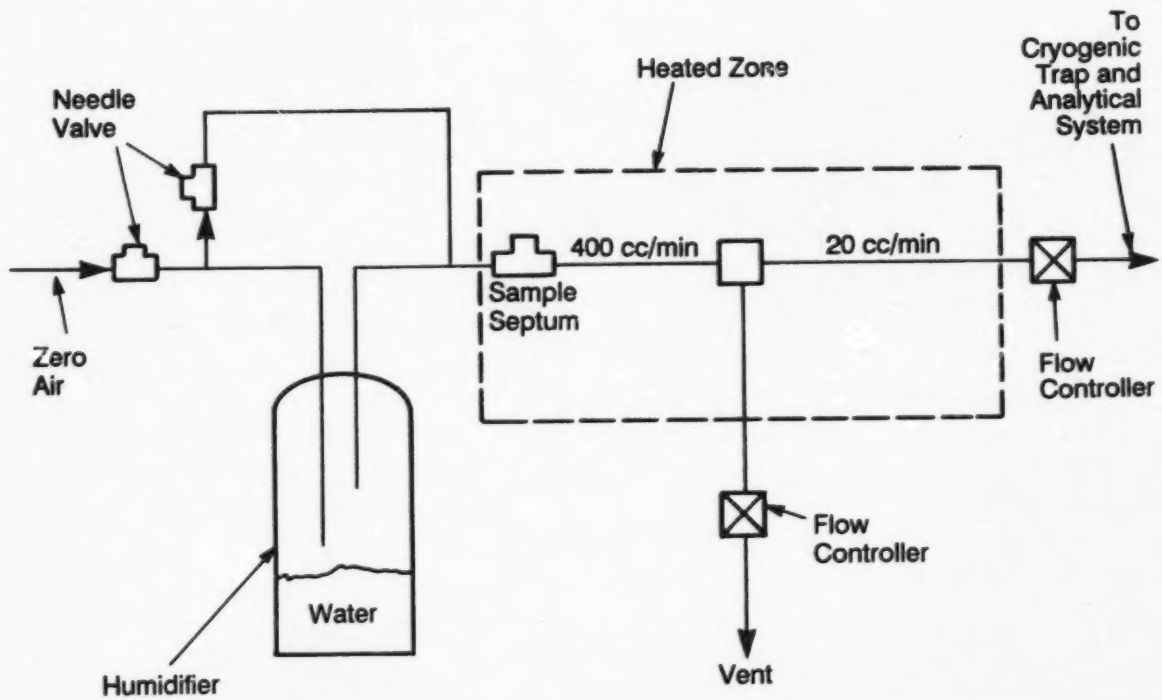

Figure 2. Delivery system for generating humidified gaseous samples.

The temperature of the column was programmed from -10°C at 10°C/min to 250°C. A problem arose when humidified samples caused ice to form in the column and block it. The problem was resolved by connecting a fused silica precolumn of larger diameter (1 m x 0.53 mm i.d.) to the analytical column inlet.

Ion Trap Detector

The quadrupole ion trap was introduced as a simple and inexpensive commercial GC detector in 1983 by Finnigan MAT. It is a fully integrated benchtop mass spectrometer with high sensitivity in both the electron impact and the chemical ionization mode. It is also capable of full cyclic scanning and selected ion monitoring.

Principle of Operation

Although based on the conventional quadrupole filter concept, the ITD, shown in Figure 3, has a totally different geometry. It consists of a central ring electrode that is located between two end-cap electrodes.[7] The gated electron beam passes through a small perforation in the upper end-cap electrode, while the ions are ejected through the perforations in the lower end-cap electrode onto the electron multiplier. A combined rf/dc voltage is applied to the central ring electrode while the two end caps are grounded.

Ion motion in the resulting three-dimensional quadrupole field is described by the Mathieu equation, which defines a stability diagram for which the ion trajectory radial components (r_o) and axial components (z_o) are stable simultaneously. In other words, in an applied rf/dc field, ions can be trapped so that their maximum displacements stay within the limits of the field-generating electrodes.[14]

Recently, a new technique for operating the ion trap was developed by Stafford and Kelley.[15] In this mass-selective instability mode, only rf voltages are applied to the central ring electrode. At a fixed frequency, the rf voltage defines the mass range that can be trapped in the field. As the rf voltage is increased, ions of increasing mass become successively unstable in the axial z direction and are ejected from the trap. These ions strike the detector and a mass spectrum is generated.

The effluent stream from the GC column flows directly into the trap through a fused silica capillary column. The pressure of the helium carrier gas is deliberately raised in order to damp the motion of the ions so that they stay in the center of the trap and are not lost to the end caps.

Electron Ionization

Figure 4 (solid lines) shows the rf voltage and timing sequence used to create ions in the trap and perform mass analysis[14-16] in the electron impact mode of operation. The initial rf voltage (level A) is chosen so that only ions in the mass range of interest are stored. The electron beam is turned on for a fixed time (typically 1 ms) to form the ions, after which the rf voltage

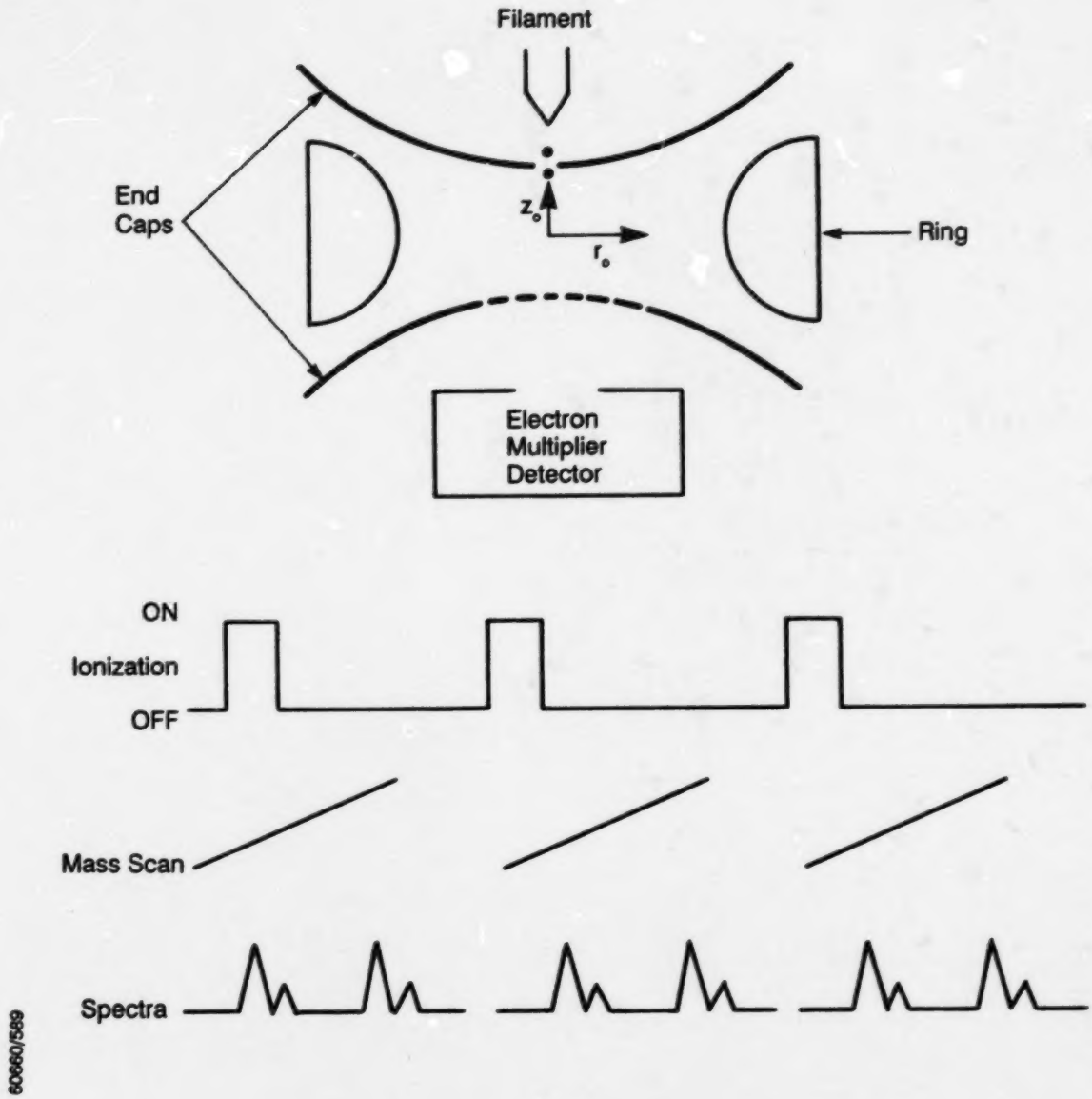

Figure 3. Schematic diagram of ion trap detector.[7]

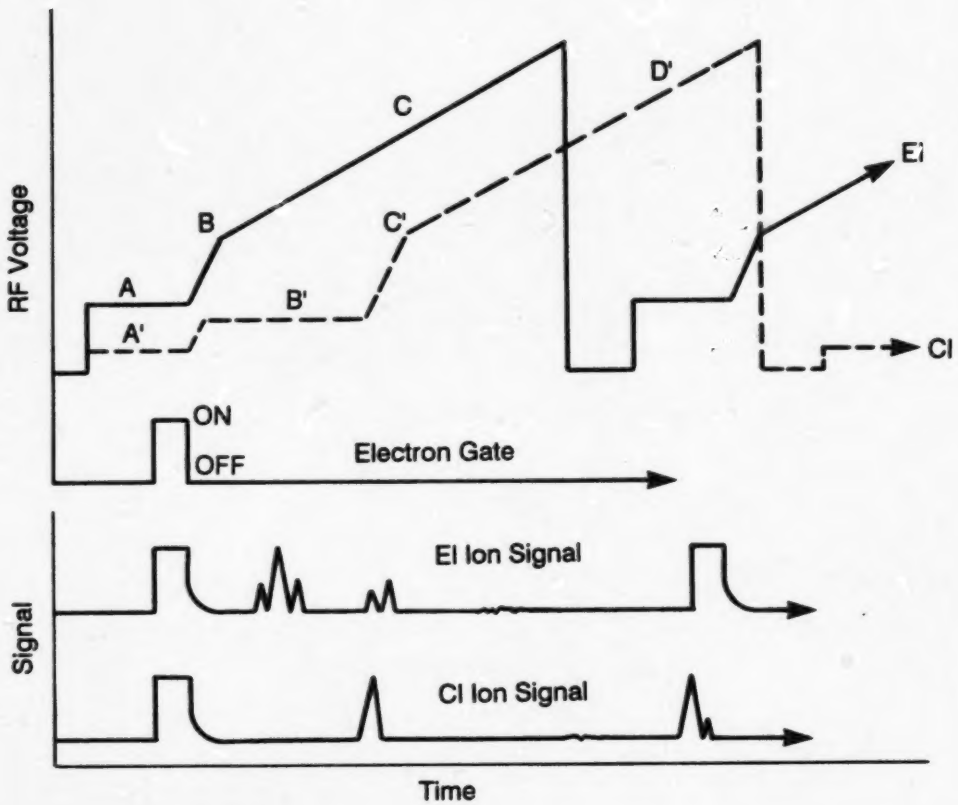

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Figure 4. Sequence of operations for obtaining either EI or CI mass spectra in the ion trap.[14-16]

is increased rapidly to a level (B) consistent with the selected low mass at which the scan is to start. As the rf voltage is ramped (C), trapped ions become successively unstable in the axial direction, in order of increasing m/z, and an EI mass spectrum is acquired.

The performance of the ITD in the EI mode has been greatly enhanced by the introduction of an Automatic Gain Control (AGC) scan function.[17] Instead of a fixed ionization time, a brief ionization pulse automatically adjusts the main ionization period (73 to 25,000 us) so as to ensure that the optimum number of ions are always produced in the ITD. This approach is designed to maximize sensitivity for low sample concentrations and prevent space-charge saturation of the trap at high concentrations.

Chemical Ionization

A chemical ionization option is also available for the ITD.[8] To operate the ion trap in the CI mode, a CI reagent gas (e.g., methane, isobutane, water, etc.) is introduced, and the sequence of rf voltages and time intervals (A' - D' in Figure 4; dashed lines) is used to create and store mass-selected reagent ions for reaction with sample molecules.[14,16]

To obtain a CI spectrum, the rf voltage is set initially at level A' for 10-20 ms in order to ionize and store CI reagent ions (ionization period). The rf voltage is then increased to level B' to eject low-mass primary ions and allow CI reagent ions to react with neutral sample molecules and form sample ions (sample reaction period). After an appropriate reaction time, the rf voltage is rapidly ramped to level C' to select the low mass for the start of the scan. The resultant CI mass spectrum is obtained (D').

It can be shown that, under the conditions that apply in the trap, the product ion current depends on:

* reagent ion intensity (ionization time)
* reaction time
* neutral sample pressure
* rate constant of the ion/molecule reaction.[18]

The Automatic Reaction Control (ARC-CI) algorithm, which is the CI analog of the AGC scan function feature in the EI mode, adjusts both the ionization time and the reaction time to form an optimum number of product ions based on the feedback from a rapid pre-scan measurement of the total ion current. The ARC-CI scan function is shown in Figure 5.

In the pre-scan segment, the rf voltage is first set to level A so that reagent gas ions can be created in the brief ionization period. The rf voltage is increased to level B to define the reaction time, which is followed by the ejection of low mass ions (level C). The total ion current is measured during period D. The reagent gas ionization time (E) and the reaction period (F) in the analytical scan segment are then set on the basis of the results of the pre-scan. This is followed by ejection of reagent ions at G, and the CI mass spectrum is finally acquired during period H.

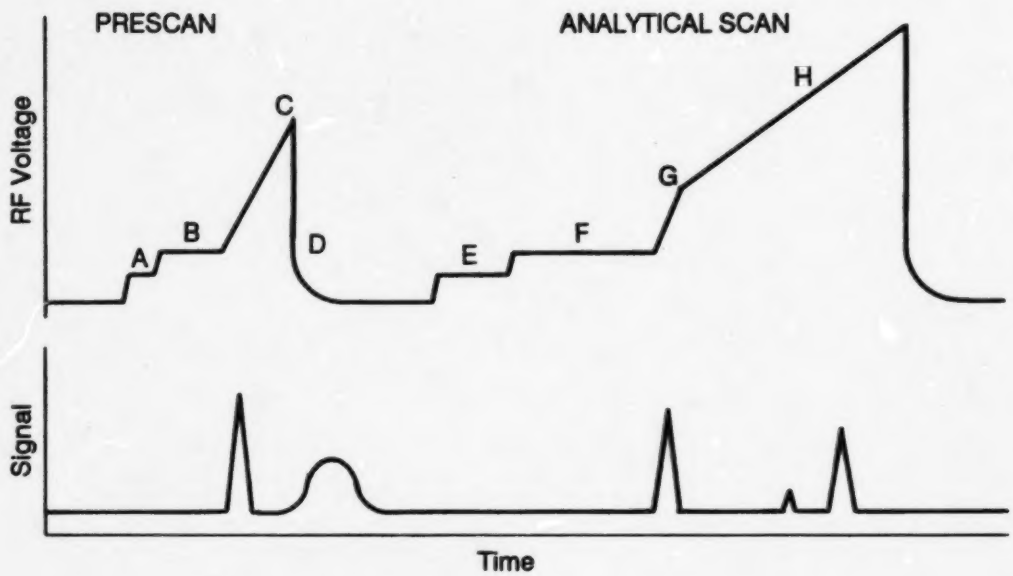

Figure 5. Diagram of scan function for CI Automatic Reaction Control (ARC).[18]

In practice, the rf amplitudes, as well as the ionization and reaction periods, are optimized for each reagent gas to maximize CI sensitivity. Reliable CI spectra depend on the proper selection of the rf voltage for reagent ion formation and storage.[8] Ionization at low rf levels gives good storage efficiency for low-mass ions, such as those commonly used as reagent gases, but not for the EI fragments from heavier sample components present in the trap at the same time. On the other hand, ionization at high rf levels suppresses the storage of reagent gas ions. The rf level should therefore be adjusted so that only the CI reagent ions of interest are stored and all other ions of higher mass are excluded.

In contrast to chemical ionization in a conventional mass spectrometer ion source, CI in the ion trap is carried out using low reagent gas pressures (ca. 10^{-5} torr), low sample pressures (low 10^{-6} torr range), and long reaction times (ca. 20 ms).[8] The reagent gas pressures are roughly an order of magnitude higher than the sample pressures; the impact of the additional water vapor on ion trap operation is therefore negligible.

CHEMICALS

Representative polar VOCs (and some nonpolar compounds) were obtained from Aldrich Chemicals. In addition, a pressurized cylinder containing ethylene oxide and propylene oxide at nominal concentrations of 10 ppmv in nitrogen was obtained from Alphagaz.

Standard solutions, prepared by diluting the neat reagents with methanol, were used to compare EI and CI fragmentation patterns. Headspace samples for injection into the sample delivery system were prepared by mixing roughly equal amounts of each compound of interest in a small flask, which was sealed with a septum cap.

PROCEDURES

Optimization of Ion Trap CI and Comparison of EI and CI Spectra

For the optimization and CI/EI comparison experiments, the cryogenic trapping unit was disconnected from the GC so that the compounds could be injected directly into the GC. Because of the variability of water vapor levels in ambient air, an externally mounted water source was used to maintain a constant reagent gas pressure for the CI experiments. The water was introduced into the ion trap from a vial attached to the reagent gas inlet port. To determine source tuning conditions, constant amounts (about 1 ng) of benzophenone were injected into the GC/CI-ITD system and the peak areas of the $(M+H)^+$ ion were measured as a function of the operating parameters. Thereafter, several representative polar species were injected into the instrument to obtain their EI and water CI mass spectra.

Trapping and Recovery Studies

Cryogenic trapping and recovery studies of several polar VOCs of interest (and some nonpolar compounds, for comparison) were carried out using the sample delivery system (Figure 2) and the cryogenic trapping unit (Figure 1) described earlier.

Using a gas-tight syringe, a fixed volume of the standard mixture was withdrawn from the flask and injected via the septum into the humidified zero-grade air stream in the sample delivery system. The VOCs were concentrated in the cryogenically cooled trap, which was maintained at -160°C by the controlled release of liquid nitrogen through a solenoid valve. The sample flow rate was set to 10 mL/min and held at this value for 10 min.

To desorb the trapped sample, the temperature of the trap was raised by removing the cryogen and rapidly heating the trap (to 200°C). At the same time, the six-port valve was switched, stopping the sample flow and directing helium carrier gas through the trap to flush the VOCs into the capillary column for GC/ITD analysis.

Several experiments were carried out under dry conditions (i.e., no water in the humidifier), and some runs were performed using humidified air with the Perma-Pure dryer between the sample delivery system and the Nutech trapping unit.

SECTION 5

RESULTS AND DISCUSSION

OPTIMIZATION OF ION TRAP CI

In general, the amount of ambient water vapor in the sample is not sufficient to provide the required level of reagent gas for efficient chemical ionization. Furthermore, the concentration of the water eluting through a capillary GC column undergoes large changes, which are dependent on the stationary phase and the temperature program used. This variability in water vapor concentration necessitates the use of a supplementary, external source of water to augment the supply and maintain a constant CI reagent level that is optimal for GC/CI-ITD analysis.

For the ion trap to operate properly in the CI mode, several operational variables must be optimized for each reagent gas[8,12]: The CI reagent gas pressure, the reagent gas ionization time and rf voltage, the sample reaction time, and the associated rf voltage. Some of these parameters were evaluated for water reagent gas by injecting fixed amounts of benzophenone into the GC/ITD system while varying one of the parameters and holding the others constant. As an example, Figure 6 shows the variation in peak area for the $(M+H)^+$ ion as a function of the ratio of the reagent gas ions *m/z* 19/18. For the remaining CI experiments described here, the reagent gas pressure was set to give a *m/z* 19/18 ratio of about 15:1, and the other operational variables were set at or near the manufacturers' recommended default values: 3.6 amu for the ionization rf level, 12 amu for the reaction rf level, 2,000 µs for the maximum reagent gas ionization time, and 100 ms for the maximum reaction time.

Since the ITD is not equipped with a pressure measuring device, the ion ratio *m/z* 19/18 was used to indicate the effect of reagent gas pressure on sample peak intensity. (Brodbelt et al.[8] attached a pressure gauge to an ion trap and showed that reagent gas pressures are typically about 10^{-5} torr for methane and isobutane). Figure 6 shows a $[19^+]/[18^+]$ ratio that is large in comparison with the ratio observed in water CI work using conventional quadrupoles.[11]

In a quadrupole system, when using water as the reagent, prominent reagent ion clusters are observed at *m/z* 19 (63% relative intensity), *m/z* 37 (100%), and *m/z* 55 (24%), corresponding to the formation of $H^+(H_2O)_n$, where n = 1, 2, and 3, respectively. In the CI mode, the ion trap shows only two reagent ions: the protonating agent H_3O^+ which occurs in significant amounts, along with H_2O^+ at *m/z* 18 which is present at much lower levels. Since the degree of solvation depends on the partial pressure of the reagent gas,[10] the absence of the larger clusters observed in quadrupole instruments is probably due to the low reagent gas pressure relative to the helium buffer gas, which is used as a damping agent in the trap.[8]

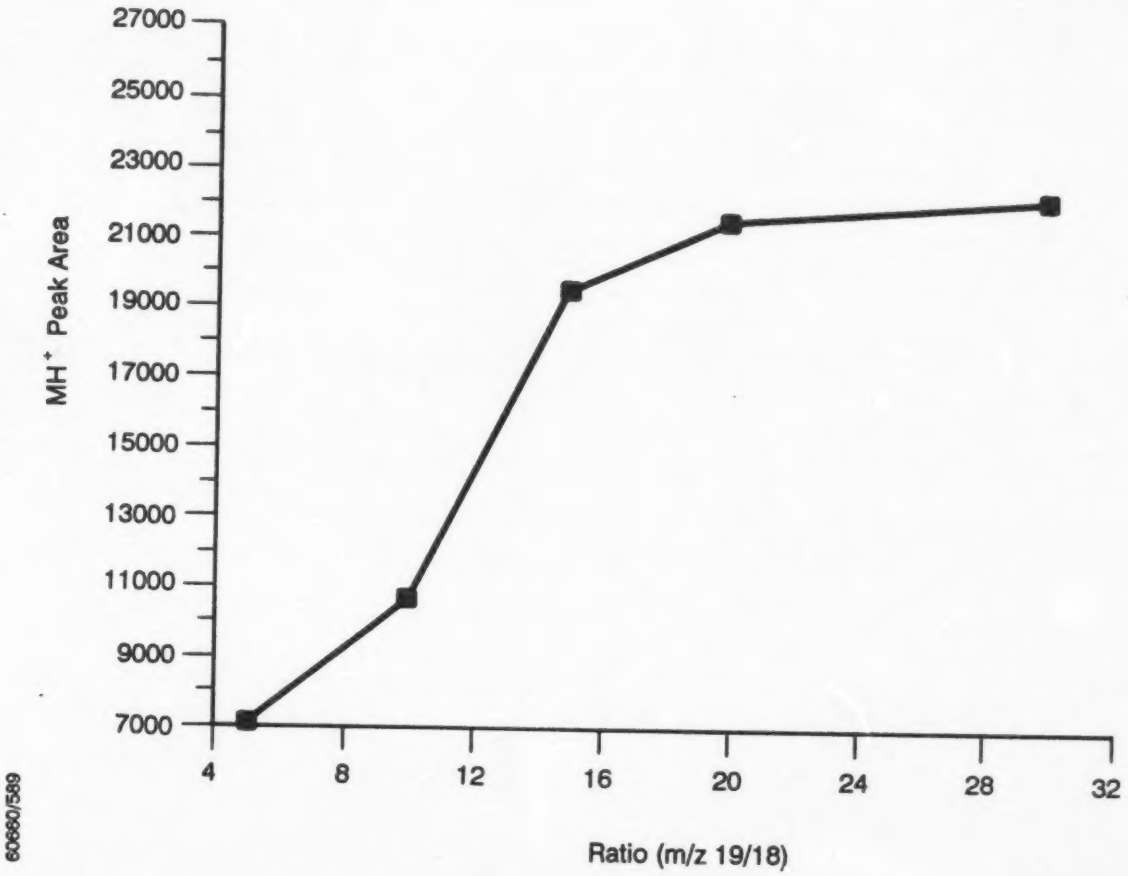

Figure 6. Effect of ratio of water reagent gas ions m/z 19/18 on peak area of $(M+H)^+$ benzophenone ion (m/z 183).

COMPARISON OF EI AND WATER CI MASS SPECTRA

The water CI and EI mass spectra of selected polar VOCs obtained using fixed operating conditions in the ion trap are summarized in Table 1. Only ions with relative abundances greater than 10% of the base peak have been included in the table. In virtually every case, the reduction in molecular ion fragmentation achieved by using water CI instead of EI is striking. Only ethanethiol shows the molecular ion as the base peak in the electron impact spectra. By contrast, all of the water CI spectra, except for amyl acetate, have the $(M+H)^+$ pseudomolecular ion as one of the major ions. Heptanal and 1-methyl-2-propanethiol are the only compounds in which the $(M+H)^+$ ion does not occur as the base peak. Since alcohols, for example, are often indistinguishable from alkanes and each other by electron impact, this illustrates a further advantage that may be derived from the use of water CI, besides the obvious advantage of being able to deal with the inherent problem of water vapor in humidified whole-air samples.

For several of these compounds, the water CI spectra have already been recorded by Hawthorne and Miller[11] using a quadrupole mass spectrometer. Table 1 also shows the base peaks obtained using the quadrupole instrument for the compounds common to the two studies. The base peaks are identified for all of the compounds for which comparisons can be made. The ion trap spectra, however, appear to undergo somewhat more fragmentation than the quadrupole spectra. This is particularly noticeable in the case of heptanal and 1-methyl-2-propanethiol. The effect is probably due to the vast differences in reaction time between the two kinds of instruments.[8]

The importance of correctly selecting operational variables, such as the ionization rf level, to obtain reliable CI spectra has been noted.[8] The data in Table 2 show that, when the ionization rf voltage is set at the default value for water (3.6 amu) to trap only H_2O^+ (m/z 18) and H_3O^+ (m/z 19), good CI spectra with intense $(M+H)^+$ ions and relatively little fragmentation are obtained. However, when the rf level is increased to 6.4 amu, sample ions of higher mass are also trapped and, although the $(M+H)^+$ ion still appears as the base peak, more extensive fragmentation is observed.

Benzophenone and naphthalene were used to compare the sensitivity of the ITD in the full cyclic scan mode under both EI and water CI conditions. For naphthalene, which undergoes very little fragmentation by either EI or water CI, the estimated limit of detection was about 0.05 ng. (The detection limit was determined by measuring the signal/noise ratio corresponding to a 1 ng sample and estimating the sample size for $S/N = 2$). For benzophenone, which fragments to a much larger extent by EI, the smallest amount of sample required to give good quality full scan mass spectra (mass range m/z 45-300) was about 0.03 ng by water CI and 0.15 ng by EI. Table 3 summarizes the total ion current ratios obtained for the injection of similar amounts of selected VOCs into the GC/ITD using water CI and EI. (Because headspace samples were used, we were unable to measure the analyte levels at which these ratios were determined.) The water CI peak areas are about 4.4 times larger than the intensities measured by EI. This observation is in fairly good agreement with results obtained by others using methane or isobutane CI.[8,12] Brodbelt et al.[8] have pointed out that this enhancement in sensitivity using CI arises largely because of the long time available for ion/molecule reactions between

TABLE 1. ION TRAP CI AND EI MASS SPECTRA OF SELECTED POLAR VOCS.

Compound	m/z	% Rel. Abundance[a]	
		Water CI	EI
Ethylene oxide	45	100	
(MW 44)	44	24	43
	43	11	14
	42		11
	29		100
3-Octanone	129	100[b]	
(MW 128)	99		35
	73		16
	72		34
	71		65
	57	10	100
	55		16
Acetophenone	121	100[b]	
(MW 120)	105	26	100
	77		41
	51		32
	50		15
	43	39	45
Benzophenone	184	13	
(MW 182)	183	100[b]	
	182		41
	181		10
	105	47	100
	77		86
	51		67
	50		29
Acrolein	57	100	
(MW 56)	55		100
	56		32
Heptanal	115	23	
(MW 114)	97	100[b]	97
	81		36
	71		18
	70	25	62
	69	17	17
	68		20
	67		18
	57	15	50
	55	46	100
	53		10
	45		22

Continued

TABLE 1. (Continued).

Compound	m/z	% Rel. Abundance[a]	
		Water CI	EI
Benzaldehyde (MW 106)	107	100[b]	17
	106		33
	105	26	100
	78		11
	77		37
	51		37
	50		20
Amyl Acetate (MW 130)	71	15	
	70		11
	61	100	15
	55		14
	43	35	100
	42		20
	41		20
	40		12
	39		15
Nitrobenzene (MW 123)	124	100	
	123		28
	93		15
	77		100
	74		12
	65		21
	51		72
	50		41
	46		13
	45		11
	44		19
	43		16
	41		16
	40		38
	39		24
	38		12
	34		14
Ethanethiol (MW 62)	63	100	14
	62	44	100
	61		18
	59		18
	58		43
	57		25
	47	39	91
	46		26
	45		67

Continued

TABLE 1. (Continued).

Compound	m/z	% Rel. Abundance[a]	
		Water CI	EI
1-Methyl-2-propanethiol (MW 90)	91	100	19
	90	29	44
	61	37	100
	49	32	21
	48	12	35
	47		36
	46		20
	45		52
	43	18	13
	41		49
	40		12
	39		45
	35		21

[a]Only ions with relative abundances ≥10% are listed.

[b]Base peak for water CI mass spectra recorded using quadrupole instrument (ref. 11).

TABLE 2. EFFECT OF IONIZATION RF LEVEL ON ION TRAP CI MASS SPECTRA

Compound	m/z	% Rel. Abundance[a]	
		3.6 amu	6.4 amu
3-Octanone (MW 128)	129	100	100
	111		35
	99		10
	73		14
	72		15
	71		88
	69		44
	59		12
	57	10	31
	47		18
	43		29
	41		11
Acetophenone (MW 120)	121	100	100
	105	26	23
	77		10
	43	39	47
Benzaldehyde (MW 106)	107	100	100
	106		10
	105	26	16
	79		20

[a]Only ions with relative abundances ≥10% are listed

TABLE 3. TOTAL ION CURRENT RATIOS OBTAINED WITH WATER CI AND EI IN THE ION TRAP

Compound	Total Ion Current Ratio CI/EI
1-Propanethiol	4.0
1-Methyl-2-propanethiol	2.0
Acetonitrile	7.6
Acrylonitrile	5.7
Tetrahydrofuran	1.2
2-Butanone	5.4
Acrolein	3.5
Ethyl acetate	2.3
Amyl acetate	5.6
Nitrobenzene	6.4
Styrene	5.2
Limonene	3.8

the reagent ions and the sample molecules. This leads to a greater accumulation of sample ions and higher sensitivity.

WATER CI-ITD ANALYSIS OF HUMIDIFIED AND DRY AIR SAMPLES

Table 4 lists the polar and nonpolar VOCs that were analyzed by water CI in the ion trap, to evaluate the effects of humidified zero-grade air, dry zero-grade air, and Perma-Pure dried air on simulated whole-air samples. The chromatographic behavior of the compounds listed was generally quite poor. This was largely because the water vapor had a significant effect upon the chromatography of the compounds, and neither the GC column nor the operating conditions were optimized for this work. Nevertheless, the experiments carried out were able to demonstrate the value of the water CI technique for the analysis of polar VOCs.

TABLE 4. POLAR AND NONPOLAR COMPOUNDS ANALYZED BY WATER CI-ITD

1-Methyl-2-propanethiol	Ethyl acetate
Acetone	Amyl acetate
2-Butanone	Nitrobenzene
Acetonitrile	Styrene
Acrylonitrile	Limonene
Acrolein	m-Dichlorobenzene
Tetrahydrofuran	

Figure 7 shows the GC/ITD profiles obtained for humidified, dry, and Perma-Pure dried air samples. Table 5 summarizes the average retention times obtained for the individual analytes, and Table 6 lists the corresponding peak areas. The effect of the water vapor in the humidified air sample on chromatographic performance is clearly shown by the elevated and wavy baseline in the total ion current profile in Figure 7(a). By contrast, the baseline is flat and essentially zero for the dry air sample (Figure 7(b)) and the Perma-Pure dried humidified air sampl (Figure 7(c)). The profile in Figure 7(c) shows, however, that the dryer also removes some of the polar compounds together with the water vapor.

Despite the effects of the water vapor on the chromatography of the compounds, Table 5 shows that relatively little retention time variability occurred in these experiments. The increased fluctuations noted with shorter retention times in the table has been observed before for nonpolar compounds,[19] and takes place when cryogenically trapped compounds including water are transferred from the trap to a capillary column held initially at a reduced temperature. Despite the use of a precolumn and a slow initial temperature program, the column is probably blocked temporarily by ice until the column temperature rises above the freezing point of the water. Since this condition is difficult to control because of the erratic character of the blocking process, the retention time fluctuations for the early eluting compounds are not unexpected.

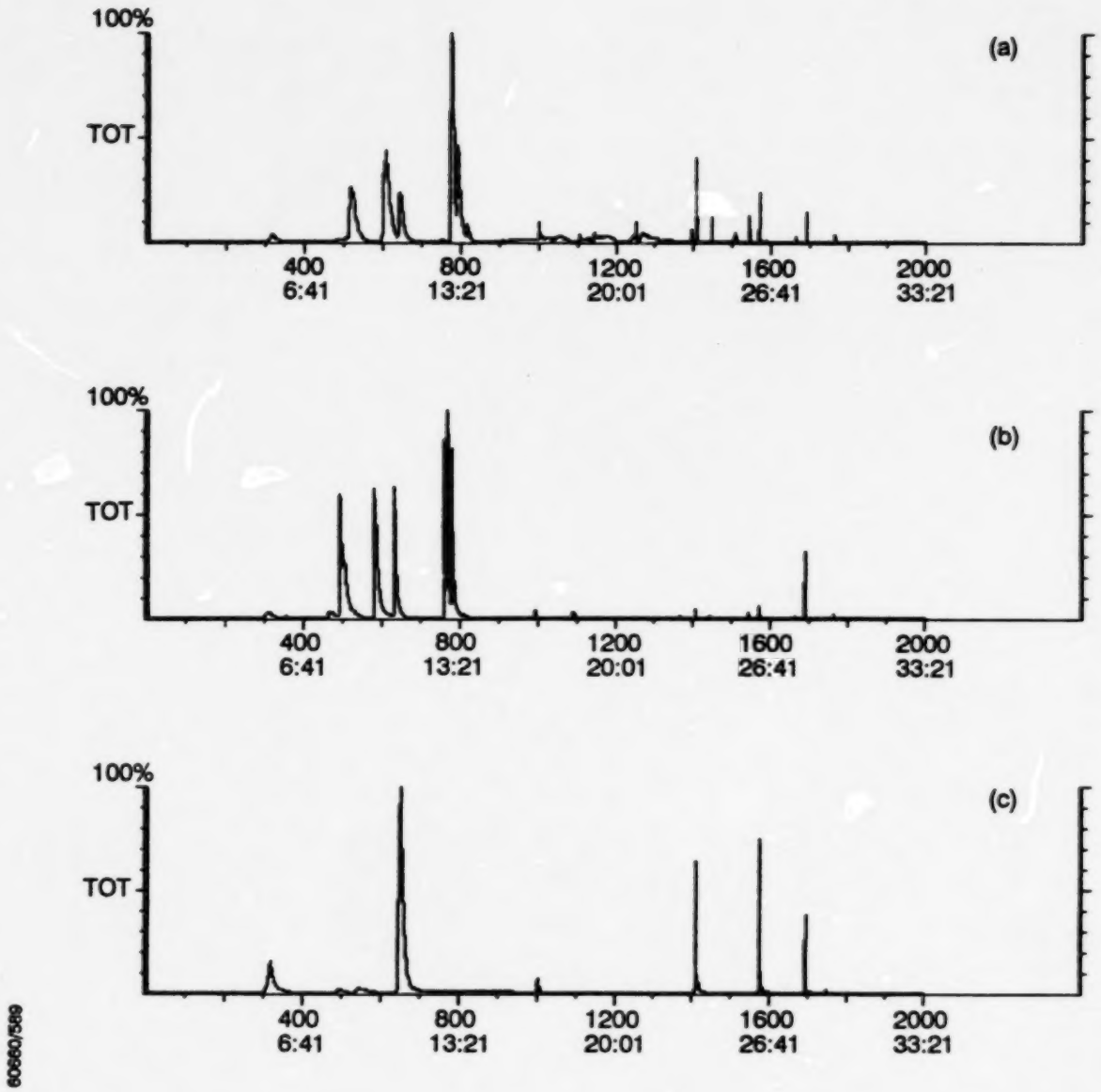

Figure 7. GC-ITD total ion current profiles using water CI of a standard mixture by cryogenic preconcentration technique: (a) humidified zero-grade air; (b) dry zero-grade air; and (c) Perma-Pure dried humidified zero-grade air.

TABLE 5. RETENTION TIMES FOR SEVERAL POLAR AND NONPOLAR VOCs CRYOGENICALLY COLLECTED AND ANALYZED BY WATER CI-ITD

Compound	Retention Time, min.		
	Humidified[a]	Dry	Perma-Pure Dried
Acetone	8.66	8.22	9.05
Acetonitrile	10.11	9.68	ND[b]
Acrylonitrile	10.73	10.55	10.83
Tetrahydrofuran	12.89	12.68	ND
Ethyl acetate	12.97	12.83	ND
2-Butanone	13.20	13.00	ND
1-Methyl-2-propanethiol	16.68	16.57	16.70
Acrolein	18.39	18.15	ND
Styrene	23.49	23.45	23.22
Amyl acetate	24.12	24.10	ND
Limonene	25.77	25.75	ND
m-Dichlorobenzene	26.21	26.18	26.25
Nitrobenzene	29.43	29.38	29.50

[a]Average of two runs

[b]ND = not detected

TABLE 6. PEAK AREAS FOR SEVERAL POLAR AND NONPOLAR VOCs CRYOGENICALLY COLLECTED AND ANALYZED BY WATER CI-ITD

Compound	Peak Area (arbitrary units)		
	Humidified[a]	Dry	Perma-Pure Dried
Acetone	7,509	18,570	70
Acetonitrile	13,398	15,871	ND[b]
Acrylonitrile	5,834	9,811	1,057
Tetrahydrofuran	3,602	7,861	ND
Ethyl acetate	12,898	11,365	ND
2-Butanone	8,695	8,706	ND
1-Methyl-2-propanethiol	523	295	30
Acrolein	141	480	ND
Styrene	1,782	3,123	99
Amyl acetate	406	92	ND
Limonene	461	151	ND
m-Dichlorobenzene	757	317	180
Nitrobenzene	157	139	ND

[a]Average of two runs

[b]ND = not detected

The effect of the Perma-Pure dryer on some of the compounds in Table 5 is striking. All of the polar compounds, with three exceptions, are removed from the gas stream along with the water vapor. The exceptions are acetone (very small peak), acrylonitrile, and 1-methyl-2-propanethiol. Both acetone and acrylonitrile are soluble in water. Thus, the small amount of acetone detected is most likely due to the fact that acetone was present at a very high level in the original mixture. The disappearance of limonene from this sample is equally surprising, since it is insoluble in water and should have passed through the dryer into the GC column, in much the same way as styrene or m-dichlorobenzene. The reasons for this aberrant behavior in the case of acrylonitrile and limonene are not understood at this time.

The effects of humidified, dry, and Perma-Pure dried air on the measured peak areas for the compounds of interest, summarized in Table 6, indicate no significant difference between the humidified and dry air samples. However, the results obtained for the Perma-Pure dried sample were significantly lower even for the nonpolar compounds, styrene and m-dichlorobenzene, which should be unaffected by the dryer. More work is needed to determine whether this behavior is due to the dryer or the result of instrument instability.

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